

AMENDMENTS TO THE SUBSTITUTE SPECIFICATION

Please amend the paragraph starting at page 1, line 8, as follows:

The present invention relates to a method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis of the concentration of sulfur in the oil sample, etc.

Please amend the paragraph starting at page 2, line 12, as follows:

The present invention was made in view of the problem in the prior art, and the object of the present invention is to provide a method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis at a minimum limit of determination of about 10 to 30 ppb by concentrating S in the oil sample by sedimentation or filtration.

Please amend the paragraph starting at page 2, line 17, as follows:

To achieve the object, a first aspect of the present invention is to provide a sulfur-capturing liquid used in the method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis to determine the concentration of sulfur in the oil sample, by removing precipitated silver acetate[[,]] and silver sulfide capturing silver compounds and silver precipitated by irradiation with electromagnetic waves or corpuscular rays, by filtration from a mixed solution of a silver nitrate solution having silver nitrate dissolved in a solvent and a sodium acetate solution having sodium acetate dissolved in the solvent if silver acetate precipitation generates unintentionally, then by irradiating the

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mixed solution with electromagnetic waves or corpuscular rays and removing precipitates containing silver sulfide by filtration if the precipitates generate.

Please amend the paragraph starting at page 2, line 26, as follows:

The present inventors found that although S should be extracted and concentrated by use of a commercial reagent in X-ray fluorescence analysis of S contained in a very small amount in an oil sample, S contained in such a commercial reagent such as solvents like C₁₋₁₈ alcohols cannot be neglected when the concentration of S in the oil sample is as very low as 10 ppb or so. Accordingly, the first aspect of this invention is a sulfur-capturing liquid from which S has been removed almost completely so as not to hinder analysis of S in a very small amount of 10 ppb or so.

Please amend the paragraph starting at page 3, line 6, as follows:

When an oil sample is ~~prepared~~ treated using the sulfur-capturing liquid in the first aspect of this invention and analyzed for S by X-ray fluorescence, S contained as an impurity in the sulfur-capturing liquid cannot be problematic, and S in a very small amount of about 10 ppb can be analyzed. This sulfur-capturing liquid is used preferably for an oil sample such as a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol, and in this case, the solvent for the sulfur-capturing liquid is preferably a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol for the sulfur-capturing

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liquid. In this invention, the oil sample as the object of analysis can be a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol. For discrimination from such oil samples, the solvent used in production of the sulfur-capturing liquid is referred to as a petroleum product for the sulfur-capturing liquid, a semi-finished petroleum product for the sulfur-capturing liquid or an alcohol for the sulfur-capturing liquid. Further, the silver compounds refer to both inorganic and organic silver compounds.

Please amend the paragraph starting at page 3, line 25, as follows:

A second aspect of this invention is a method of producing the sulfur-capturing liquid in the first aspect of this invention, and follows the procedures described below. First, a silver nitrate solution having silver nitrate dissolved in a solvent is mixed with a sodium acetate solution having sodium acetate dissolved in the solvent~~[[,]] to form silver acetate.~~ [[Then]] If silver acetate precipitate generates unintentionally, the mixed solution is subjected to a first filtration to remove the silver acetate. Then, the solution is irradiated with electromagnetic waves or corpuscular rays ~~to precipitate silver sulfide-containing silver compounds and silver.~~ If at least one of the silver nitrate solution and the sodium acetate solution contains sulfur compounds, precipitates containing silver sulfide generates. Then, the solution is subjected to a second filtration to remove the silver compounds and silver. Then, a nitrogen gas is allowed to flow into the solution to remove dissolved oxygen. Finally, an aldehyde or ammonia is added for preventing oxidation and improving the long-term shelf life.

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Please amend the paragraph starting at page 5, line 13, as follows:

A fourth aspect of this invention is a method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis of the concentration of sulfur in the oil sample, and follows the procedures described below. First, a nitrogen gas is allowed to flow into the sulfur-capturing liquid in the first aspect of this invention to remove dissolved oxygen. Then, the sulfur-capturing liquid is added to the oil sample collected in a sample holder and then stirred. Then, the stirred solution is irradiated with electromagnetic waves or corpuscular rays to precipitate silver sulfide-containing silver compounds and silver. Then, ammonia or an aldehyde is further added to dissolve silver compounds and silver other than silver sulfide-containing sulfur compounds, whereby the silver sulfide-containing sulfur compounds are left as precipitates on a window in the bottom of the sample holder.

Please amend the paragraph starting at page 5, line 26, as follows:

According to the fourth aspect of this invention, the sulfur-capturing liquid from which S was almost completely removed according to the first aspect of this invention is used whereby S contained in the oil sample is extracted, sedimented and concentrated, and therefore fluorescent X-ray intensity enough to measure S can be obtained to analyze S in a very small amount of about 10 ppb. The method of ~~preparing~~ capturing sulfur in the oil sample is used preferably for an oil sample such as a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈

alcohol, and in this case, the solvent in the sulfur-capturing liquid is preferably a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol for the sulfur-capturing liquid. Further, as the electromagnetic waves or corpuscular rays, may be employed X-rays having longer wavelengths than the L absorption edge wavelength of silver and containing the absorption edge wavelength of sulfur.

Please amend the paragraph starting at page 6, line 14, as follows:

A fifth aspect of this invention is an X-ray fluorescence spectrometer for analyzing the concentration of sulfur in an oil sample by the ~~preparation~~ method in the fourth aspect of this invention, which comprises a pretreatment X-ray source for downward irradiating the stirred solution with the electromagnetic waves or corpuscular rays and an analytical X-ray source for upward irradiating a window in the bottom of the sample holder with primary X-rays.

Please amend the paragraph starting at page 7, line 10, as follows:

A sixth aspect of this invention is a method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis of the concentration of sulfur in the oil sample, and follows the procedures described below. First, a nitrogen gas is allowed to flow into the sulfur-capturing liquid in the first aspect of the invention to remove dissolved oxygen. Then, the sulfur-capturing liquid is added to the oil sample and then stirred.

Then, the stirred solution is irradiated with electromagnetic waves or corpuscular rays

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and further filtered through a filter membrane, to separate silver sulfide-containing sulfur compounds and silver on the filter membrane.

Please amend the paragraph starting at page 7, line 20, as follows:

According to the ~~preparation~~ method in the sixth aspect of the invention, the sulfur-capturing liquid from which S was almost completely removed according to the first aspect of the invention is used whereby S contained in the oil sample is extracted, filtered and concentrated, and therefore fluorescent X-ray intensity enough to measure S is obtained, but unlike the ~~preparation~~ method in the fourth aspect of the invention, re-dissolution of precipitates other than sulfur compounds is not conducted. Accordingly, the minimum limit of determination is made about 15 ppb, but a very small amount of S can also be analyzed and the measurement sample can be prepared rapidly and easily. Further, unlike the ~~preparation~~ method in the fourth aspect of the invention, S contained in the oil sample is concentrated by filtration, and thus the measurement sample can be prepared more rapidly without waiting sedimentation, and further S contained in the oil sample is not precipitated on the window in the bottom of the sample holder, but separated and stuck as solid on the filter membrane, and can thus be analyzed by the X-ray fluorescence spectrometer for not only upward but also downward irradiation. This method of ~~preparing the~~ capturing sulfur in an oil sample can be used preferably for an oil sample such as a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol, and in this case, the solvent in the sulfur-capturing liquid is preferably a petroleum product, a semi-finished petroleum

product serving as the starting material thereof or a C₁₋₈ alcohol for the sulfur-capturing liquid. Further, as the electromagnetic waves or corpuscular rays, may be employed X-rays having longer wavelengths than the L absorption edge wavelength of silver and containing the absorption edge wavelength of sulfur.

Please amend the paragraph starting at page 8, line 19, as follows:

A seventh aspect of the invention is a method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis of the concentration of sulfur in the oil sample, and follows the procedures described below. First, a silver nitrate solution having silver nitrate dissolved in a solvent and a sodium acetate solution having sodium acetate dissolved in the solvent are added as a sulfur-capturing liquid to the oil sample collected in a sample holder and then stirred. Then, the stirred solution is irradiated with electromagnetic waves or corpuscular rays to precipitate silver sulfide-containing silver compounds and silver on a window in the bottom of the sample holder.

Please amend the paragraph starting at page 9, line 1, as follows:

According to the ~~preparation~~ method in the seventh aspect of the invention, S contained in the oil sample is extracted, sedimented and concentrated, and therefore fluorescent X-ray intensity enough to measure S is obtained, but unlike the ~~preparation~~ method in the fourth aspect of the invention, removal of S contained in the reagents and re-dissolution of precipitates other than sulfur compounds are not conducted.

Accordingly, the minimum limit of determination is made about 30 ppb, but a small

amount of S can also be analyzed and the measurement sample can be prepared rapidly and easily. This method of ~~preparing~~ capturing sulfur in the oil sample can also be used preferably for an oil sample such as a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol, and in this case, the solvent in the sulfur-capturing liquid is preferably a C₁₋₈ alcohol for the sulfur-capturing liquid. Further, as the electromagnetic waves or corpuscular rays, may be employed X-rays having longer wavelengths than the L absorption edge wavelength of silver and containing the absorption edge wavelength of sulfur, or X-rays monochromated in the absorption edge wavelength of sulfur.

Please amend the paragraph starting at page 9, line 20, as follows:

An eighth aspect of the invention is a method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis of the concentration of sulfur in the oil sample, and follows the procedures described below. First, a silver nitrate solution having silver nitrate dissolved in a solvent and a sodium acetate solution having sodium acetate dissolved in the solvent are added as a sulfur-capturing liquid to the oil sample and then stirred. Then, the stirred solution is irradiated with electromagnetic waves or corpuscular rays and further filtered through a filter membrane to separate silver sulfide-containing silver compounds and silver on the filter membrane.

Please amend the paragraph starting at page 10, line 1, as follows:

According to the ~~preparation~~ method in the eighth aspect of the invention, S contained in the oil sample is extracted, filtered and concentrated, and therefore fluorescent X-ray intensity enough to measure S is obtained, but like the ~~preparation~~ method in the seventh aspect of the invention, removal of S contained in the reagents and re-dissolution of precipitates other than sulfur compounds are not conducted. Accordingly, the minimum limit of determination is made about 30 ppb, but a small amount of S can also be analyzed and the measurement sample can be prepared rapidly and easily. Further, unlike the ~~preparation~~ method in the seventh aspect of the invention, S contained in the oil sample is concentrated by filtration, and thus the measurement sample can be prepared more rapidly without waiting sedimentation, and further S contained in the oil sample is not precipitated on the window in the bottom of the sample holder, but separated and stuck as solid on the filter membrane, and can thus be analyzed by the X-ray fluorescence spectrometer for not only upward but also downward irradiation. This method of ~~preparing~~ capturing sulfur in the oil sample can also be preferably used for an oil sample such as a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol, and in this case, the solvent in the sulfur-capturing liquid is preferably a C₁₋₈ alcohol for the sulfur-capturing liquid. Further, as the electromagnetic waves or corpuscular rays, may be employed X-rays having longer wavelengths than the L absorption edge wavelength of silver and containing the absorption edge wavelength of sulfur, or X-rays monochromated in the absorption edge wavelength of sulfur.

Please amend the paragraphs from page 12, line 5 to page 13, line 6, as follows:

Figs. 1A and 1B show in combination a flowchart of a method of producing a sulfur-capturing liquid used in the method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis in a first embodiment of this invention.

Fig. 2 is a flowchart showing the method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis in the first embodiment of this invention.

Fig. 3 is an illustration showing one example of an X-ray fluorescence spectrometer for analyzing the concentration of sulfur in an oil sample by the ~~preparation~~ method.

Fig. 4 is one example of the calibration curve prepared by the ~~preparation~~ method.

Fig. 5 is a flowchart showing the X-ray fluorescence analysis method in the third embodiment of this invention.

Fig. 6 shows one example of the calibration curve prepared by the analysis method.

Fig. 7 is a schematic sectional view showing suction filtration in the method of ~~preparing~~ capturing sulfur in an oil sample for X-ray fluorescence analysis in the second or fourth embodiment of this invention.

Fig. 8 is a schematic sectional view showing X-ray fluorescence analysis of a material separated on a filter membrane by suction filtration in the ~~preparation~~ method.

Fig. 9 is a schematic sectional view showing pressure filtration in place of suction filtration in the ~~preparation~~ method.

Fig. 10 is a schematic sectional view showing a material separated on a filter membrane by pressure filtration in the ~~preparation~~ method.

Fig. 11 is a schematic sectional view showing X-ray fluorescence analysis of a material separated on a filter membrane by pressure filtration in the ~~preparation~~ method.

Please amend the paragraph starting at page 13, line 9 as follows:

Hereinafter, the first embodiment of the invention, that is, the method of ~~preparing~~ capturing sulfur in an oil sample (corresponding to the fourth aspect of the invention) is described. This ~~preparation~~ method is a method of ~~preparing~~ capturing sulfur in an oil sample such as a petroleum product, a semi-finished product or C₁₋₈ alcohol for X-ray fluorescence analysis of the concentration of sulfur in the oil sample, and in this method, a sulfur-capturing liquid is used. This sulfur-capturing liquid is an embodiment corresponding to the first aspect of the invention, which is prepared by removing silver acetate, and silver sulfide-containing silver compounds and silver precipitated by irradiation with electromagnetic waves or corpuscular rays, by filtration from a mixture of a silver nitrate solution having silver nitrate dissolved in a solvent and a sodium acetate solution having sodium acetate dissolved in the solvent.

Please amend the paragraph starting at page 16, line 19 as follows:

In the method of ~~preparing~~ capturing sulfur in an oil sample in this embodiment, the procedures shown in the flowchart in Fig. 2 are followed as described below using the sulfur-capturing liquid thus prepared. First, a nitrogen gas is allowed to flow into the sulfur-capturing liquid to remove dissolved oxygen. This is to prevent silver oxide from occurring later due to oxygen dissolved during storage. In this example, the sulfur-capturing liquid is bubbled for 20 minutes (step 1).

Please amend the paragraph starting at page 20, line 20 as follows:

Fig. 4 shows a calibration curve prepared by preparing 5 kinds of standard oil samples whose standard values of S were 0, 25, 50, 75 and 100 ppb by the ~~preparation~~ method in this embodiment and then analyzing the concentrations of S therein, wherein the sulfur-capturing liquid was produced using the conventional downward irradiating X-ray fluorescence spectrometer, and the oil samples were prepared and analyzed using the conventional upward irradiating X-ray fluorescence spectrometer. Although the concentrations of S are as very low as several 10 ppb levels, a considerably linear calibration curve can be prepared. Then, 10 oil samples in sample holders ($n = 1$ to 10) were prepared in the same manner as for the standard oil samples by diluting DBDS ($C_4H_9-S-S-C_4H_9$) with isopropanol to adjust the concentration of S to 50 ppb, and using the ~~preparation~~ method in this embodiment by, and the concentration of S in these oil samples was analyzed by reference to the above calibration curve. The result is shown in Table 1. As can be seen from this result, repeatability as high as a σ value of 5.15

and a CV value of 9.6 can be achieved although the concentration of S is as very low as 50 ppb (0.05 ppm).

Please amend the paragraph starting at page 21, line 12 (after the Table) as follows:

According to the method of ~~preparing~~ capturing sulfur in an oil sample in the first embodiment as described above, the sulfur-capturing liquid 15 from which S was almost completely removed is used whereby S contained in the oil sample 16 is extracted, sedimented and concentrated as a silver sulfide-containing sulfur compound 18, and therefore S in a very small amount of about 10 ppb can be analyzed.

Please amend the paragraph starting at page 22, line 2 as follows:

Now, the method of ~~preparing~~ capturing sulfur in an oil sample in the second embodiment of the invention (corresponding to the sixth aspect of the invention) is described. This method of ~~preparing~~ capturing sulfur in an oil sample is the same as the method of ~~preparing~~ capturing sulfur in an oil sample in the first embodiment (corresponding to the fourth aspect of the invention) until the sulfur-capturing liquid is added to an oil sample collected in a container, and they are stirred to be irradiated with X-rays as the electromagnetic waves or corpuscular rays. In this embodiment, it is to be noted that the container for collecting the oil sample may be any one in which the sulfur-capturing liquid added can be stirred and irradiated with X-rays, so the container is not limited to the liquid sample container (sample holder 11 in Fig. 3) for X-ray fluorescence

analysis. As the X-rays used for irradiation to the stirred solution, are employed X-rays containing the absorption edge wavelength (5.018 Å) of sulfur, which are irradiated downward as primary X-rays by the conventional downward irradiating X-ray fluorescence spectrometer.

Please amend the paragraph starting at page 24, line 6 as follows:

In the method of ~~preparing~~ capturing sulfur in an oil sample in the second embodiment, filtration may be conducted by pressure filtration. For example, as shown in Fig. 9, the solution 28 irradiated with the X-rays is sucked in a syringe 32, and a filtration cartridge 33 having the filter membrane 26 integrated therein is attached to the top of the syringe 32, and the solution 28 in the syringe 32 is pushed out for pressure filtration. The filter membrane 26 may be the same as in suction filtration. As a result of pressure filtration, silver sulfide-containing silver compounds and silver 27 are separated on the filter membrane 26 as shown in Fig. 10. That is, S contained in the oil sample is concentrated and coated as a part of the separated material on the filter membrane 26 in the filtration cartridge 33, and this filtration cartridge 33 is disassembled to remove the filter membrane 26, and as shown in Fig. 11, the filter membrane 26 is integrated into a sample holder (referred to hereinafter as solid sample holder) 34 used for conventional solid samples, and then mounted on a sample stand in the downward-irradiating X-ray fluorescence spectrometer so that the intensities of the fluorescent X-rays 7 emitted upon downward irradiation to the separated material 27 with primary X-rays 6 can be measured. Alternatively, while the solid sample holder 34

is in a downward direction, the separated material 27 can be analyzed in the same manner as in suction filtration by the upward irradiating X-ray fluorescence spectrometer. Further, filtration may be conducted easily by filtration at normal pressure with a similar filtration member 26 although the filtration time is prolonged.

Please amend the paragraph starting at page 25, line 3 as follows:

According to the method of ~~preparing~~ capturing sulfur in an oil sample in the second embodiment as described above, the same sulfur-capturing liquid as in the first embodiment, from which S was removed almost completely, is used whereby S contained in the oil sample is extracted, filtered and concentrated thus giving fluorescent X-ray intensity enough to measure S, but unlike the ~~preparation~~ method in the first embodiment, re-dissolution of precipitates other than sulfur compounds is not conducted. Accordingly, the minimum limit of determination is made about 15 ppb, but a very small amount of S can also be analyzed and the measurement sample can be prepared rapidly and easily. Further, unlike the ~~preparation~~ method in the first embodiment, S contained in the oil sample is concentrated by filtration and can thus be prepared more rapidly without waiting sedimentation, and S contained in the oil sample is not precipitated on the window (downward in the solution) in the bottom of the sample holder (liquid sample holder), but separated and stuck as solid on the filter membrane, and can thus be analyzed by the X-ray fluorescence spectrometer for not only upward but also downward irradiation.

Please amend the paragraph starting at page 25, line 21 as follows:

Then, the X-ray fluorescence analysis method in the third embodiment of the invention (corresponding to the ninth aspect of the invention) is described by reference to the flowchart in Fig. 5. This X-ray fluorescence analysis method includes an embodiment of the method of ~~preparing~~ capturing sulfur in an oil sample in the seventh aspect of the invention. In this X-ray fluorescence analysis method, a silver nitrate solution having silver nitrate dissolved in a solvent and a sodium acetate solution having sodium acetate dissolved in the solvent are added as the sulfur-capturing liquid to the oil sample collected in the sample holder and then stirred. When the oil sample is a petroleum product, a semi-finished petroleum product serving as the starting material thereof or a C₁₋₈ alcohol, the solvent in the sulfur-capturing liquid is preferably a C₁₋₈ alcohol for the solvent. In this example, isopropanol (isopropyl alcohol) easily available is used as the solvent.

Please amend the paragraph starting at page 28, line 2 (after the Table) as follows:

In the X-ray fluorescence analysis method in the third embodiment as described above, S contained in the oil sample is extracted, sedimented and concentrated thus giving fluorescent X-ray intensity enough to measure S, but unlike the ~~preparation~~ method in the first embodiment, removal of S contained in the reagents and re-dissolution of precipitates other than sulfur compounds are not conducted. Further, the conventional upward irradiating X-ray fluorescence spectrometer can be used in both

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irradiation of X-rays for preparation (pretreatment) and irradiation of primary X-rays for analysis of the oil sample prepared. Accordingly, S in a very small amount of about 30 ppb can be analyzed rapidly and easily.

Please amend the paragraph starting at page 28, line 14 as follows:

Now, the method of ~~preparing~~ capturing sulfur in an oil sample in the fourth embodiment of this invention (corresponding to the eighth aspect of the invention) is described. This method of ~~preparing~~ capturing sulfur in an oil sample is the same as the method of ~~preparing~~ capturing sulfur in an oil sample (used in the X-ray fluorescence analysis method in the third embodiment) in the seventh aspect of the invention until the sulfur-capturing liquid is added to an oil sample collected in the container, and they are stirred to be irradiated with X-rays as the electromagnetic waves or corpuscular rays. However, the irradiation with X-rays for preparation (pretreatment) is not carried out simultaneously with the irradiation with primary X-rays for analysis of the oil sample prepared, so it is not necessary that the container for collection of the oil sample is a liquid sample container (sample holder 11 in Fig. 3) for X-ray fluorescence analysis. In this example, as the X-rays used for irradiation to the stirred solution, are employed primary X-rays containing the absorption edge wavelength (5.018 Å) of sulfur, which are irradiated downward by the conventional downward irradiating X-ray fluorescence spectrometer. In the same manner as in the ~~preparation~~ method in the second embodiment, the solution irradiated with the X-rays is filtered through a filter

membrane under suction, under pressure or at normal pressure, to separate silver sulfide-containing silver compounds and silver on the filter membrane.

Please amend the paragraph starting at page 29, line 19 as follows:

In the method of ~~preparing~~ capturing sulfur in an oil sample in the fourth embodiment, S contained in the oil sample is extracted, filtered and concentrated thus giving fluorescent X-ray intensity enough to measure S, but like the X-ray fluorescence analysis method in the third embodiment, removal of S contained in the reagents and re-dissolution of precipitates other than sulfur compounds are not conducted. Further, S contained in the oil sample is concentrated by filtration, thus eliminating the time necessary for sedimentation. Accordingly, S in a very small amount of about 30 ppb can be analyzed rapidly and easily. Further, S contained in the oil sample is not precipitated on the window (downward in the solution) in the bottom of the sample holder (liquid sample holder), but separated and stuck as solid on the filter membrane, and can thus be analyzed by the X-ray fluorescence spectrometer for not only upward but also downward irradiation.